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## A16

### ADVANCED TECHNIQUES FOR MOBILE MONITORING OF TRACE ORGANICS IN AIR

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The measurement of trace organic compounds in air poses several challenges to the analytical chemist. Often the compounds of interest are present at trace levels, for short, irregular time periods, in a complex chemical matrix. Since the early 1970's, the Air Resources Branch has recognized the need for state-of-the-art mobile laboratories to gather vital air quality data near the source in the affected community. The original mobile air monitoring units (MAMUs) were equipped to measure only a few classical pollutants, namely: sulphur dioxide, oxides of nitrogen, and carbon monoxide. Owing to the recent advances in analytical instrumentation and an enhanced awareness of volatile organic contaminants, the monitoring capabilities of the MAMUs have been vastly expanded. Today the Ministry operates four MAMUs which provide on-site measurements of a broad range of volatile organic and inorganic compounds. Our latest addition to the MAMU fleet is the mobile TAGA 6000E - a tandem mass spectrometer with real-time, direct air analyses. Supplementing the MAMUs are our lab-based instruments for verification of pollutant identities: an isolation matrix FTIR, triple column GC/MSD, and a dual oven GC. The MAMUs' unique capabilities have proven to be invaluable to the Ministry in a variety of monitoring applications: from tracking plumes of toxic gases in a small community to assisting the Ministry personnel in clean-up operations of chemical spills.

## Introduction

The Ministry of Environment (MOE) has been responsible for the protection and assurance of air quality in Ontario since 1968. By the late seventies, the Ministry operated a network of over 125 permanent air monitoring stations throughout Ontario. While this fixed network system serves an adequate surveillance function, it can not respond as efficiently as major environmental problems merit. The Air Resources Branch, which provides specialized services and manages various programs to support the Ministry's mandate, developed a mobile air monitoring system. Today, the Ministry operates four world-class Mobile Air Monitoring Units (MAMUs) throughout Ontario, backed up by a dedicated team of scientists and technicians. These units are completely self-contained mobile air monitoring laboratories that can be dispatched to any area of the Province of Ontario to quickly determine relevant air quality parameters.

## Background

The Ministry of Environment started with mobile air monitoring in 1970 on a very modest scale. The first mobile air monitoring unit, a Ford station wagon with a Sign X SO<sub>2</sub> analyzer, was used extensively for the monitoring of SO<sub>2</sub> pollution in the area of Sudbury, prompted by the construction of the INCO superstack. Soon the demand for mobile monitoring went beyond SO<sub>2</sub>, to include THC, CO, H<sub>2</sub>S, O<sub>3</sub> and Hg. Out of this demand came the second mobile air monitoring unit, a Ford Econoline van. For the first time, power to the scientific instrumentation was supplied either from a shore line or by an onboard generator. The data were recorded by a six-channel line recorder and later manually evaluated in the laboratory - an extremely laborious task, as four weeks were required to interpret one week of data. The first data acquisition system from Hewlett-Packard was a vast improvement, as now all the data could be punched simultaneously onto a single paper tape, and then read at home base into an HP9830 computer.

Around 1975, it became obvious that a larger mobile air monitoring platform was needed to accomplish the tasks required of the unit, as available space in the small Ford Econoline van was by this time substantially limited. A GMC Transmode was eventually chosen as the replacement, and in 1976 the new generation of mobile air monitoring units was born with the introduction of MAMU 1. In 1981 the second MAMU was commissioned to address the increased number of survey requests. MAMUs 1 and 2 have similar capabilities, and, in addition to monitoring common pollutants, they routinely measure up to 133 distinct volatile organic compounds using advanced gas chromatographic techniques.

As the emphasis in mobile air monitoring shifted from the measurement of common inorganic pollutants to the more elusive trace organics, the Ministry examined new technology and, in 1978,

acquired a mobile TAGA 3000. Developed in Ontario by SCIEX Inc., the TAGA (Trace Atmospheric Gas Analyzer) is a specialized mass spectrometer with direct air analysis capabilities. This unit later became known as MAMU 3. Finally, in August 1987, the Air Resources Branch added a fourth mobile air monitoring unit to their fleet: MAMU 4. This unit, converted from an Orion bus, contains a significantly improved version of the TAGA 3000 - a tandem mass spectrometer (MS/MS) - TAGA 6000. Both of these units are capable of real time detection and monitoring of a wide range of organic and inorganic compounds. MAMU 4 (TAGA 6000) has the added capability of identifying unknown pollutants in a matter of seconds. MAMUs 3 and 4 are adept at tracking down fugitive emissions and locating the precise source of pollutants.

#### MAMUs 1 and 2

MAMUs 1 and 2 are housed in GMC Transmode vehicles which are both stylish and practical. The vehicles are characterized by a smooth, low vibration ride due to a self-levelling air bag and torsion bar suspension system. The front wheel drive vehicles provide sufficient flat floor space to accommodate the scientific and monitoring instrumentation. Schematics of MAMU 1 floor plans are shown in Figure 1a.

Each unit is powered by two six-kilowatt generators with electronic frequency controllers. Two independent circuits permit electrical isolation of sensitive scientific instrumentation from the auxiliary equipment. Since each generator can supply power to either circuit, analytical equipment can remain functional in an emergency monitoring situation should a generator fail.

Each MAMU represents a capital expenditure of nearly one million dollars. Thus they are equipped with fire, vandalism, and power loss sensors. A two-way radio system with a unique frequency, plus a cellular phone provides the MAMUs with a communication link with each other and with the Air Resources Branch.

Since the measurement of meteorological data is of paramount importance in air pollution studies, the MAMUs are outfitted with meteorological instruments that continuously record wind speed and direction, temperature, humidity, solar radiation and barometric pressure. Minisondes and automated dual theodolite tracking systems are included in MAMUs 1 and 2. The simultaneous acquisition of meteorological parameters and air quality data is essential for source delineation.

#### Common Pollutants Instrumentation

MAMUs 1 and 2 are equipped with several discrete analyzers to measure the common, or classical, pollutants on a continuous basis. Instrumentation common to both MAMUs include the following:

- a dual flame ionization analyzer to measure total

- hydrocarbons, non-methane hydrocarbons and methane
- a filter correlation spectrometer for monitoring carbon monoxide
- a chemiluminescent, dual channel analyzer to monitor nitrogen monoxide and nitrogen dioxides
- a fluorescent sulfur dioxide analyzer which serves two purposes: the measurement of sulfur dioxide; and the measurement of total reduced sulfur compounds
- an ultraviolet absorption ozone analyzer

In addition to the above analyzers, MAMU 2 contains an ultraviolet spectrometer for the detection of elemental mercury, and a second sulfur dioxide analyzer. Utilizing the SO<sub>2</sub> analyzers, one with a SO<sub>2</sub> scrubber and a high temperature converter system, permits simultaneous measurements of SO<sub>2</sub> and TRS.

The functions of data acquisition, span and zero for all instruments are under computer control (HP 9886). Thus, once the instruments have been calibrated and set in the monitoring mode, air quality data are automatically recorded and reported every 30 seconds. Later the data are transferred to a main frame computer for further data reduction and analysis.

#### Volatile Organic Compounds (VOCs)

Both MAMUs 1 and 2 utilize identical GC systems developed by the Air Resources Branch laboratory. Volatile organic contaminants are sampled onto a multi-component adsorbent cartridge from a 3 litre air sample. Following thermal desorption, contaminants are focused onto low volume loops cooled to liquid nitrogen temperatures. Then the contaminants are identified using a sophisticated GC (HP 5880) with two high resolution capillary columns of different polarity (DB 1 and DB 5), each coupled to a flame ionization detector. The identification of pollutants is based on a library of retention indices. Pollutants must be confirmed on both columns to be reported as present. The basic components of this system are depicted in Figure 2.

Currently the system is calibrated for 133 hydrocarbons with three to twelve carbon atoms. The following chemical classes are represented: alkanes, alkenes, alkynes, aromatics and chlorinated hydrocarbons. Detection limits are typically in the range of 1 to 5 ug/l for a 3 litre sample. A detailed list of all the pollutants targeted by MAMUs 1 and 2 is presented in Table 1.

#### MAMU 3 (TAGA 3000) and MAMU 4 (TAGA 6000)

The GCs of MAMUs 1 and 2 can monitor a predetermined number of non-polar hydrocarbons which comprise the retention index library. Owing to the presence of the Nafion perma-pure dryers, the GCs are not conducive to the measurement of polar organics which are more reactive, and therefore subject to alteration during

sampling and analysis.

On the other hand, the unique TAGA technology of MAMUs 3 and 4 are adept at monitoring ultra-trace levels in complex air matrices. The TAGA is a specialized quadrupole mass spectrometer with an atmospheric pressure, chemical ionization (APCI) ion source that accepts air samples in their original composition. This direct analytical approach circumvents problems associated with conventional trapping methods. The basic features of the TAGA system are shown in Figure 3. Airborne contaminants are sampled directly into the APCI source at high flow rates of five l/sec assuring minimal memory effects. Pollutants are electrically charged via chemical ionization reactions initiated by a corona discharge. Selective detection of chemical classes is accomplished through the addition of the appropriate chemical ionization reagent, for example, benzene is added to the ambient air stream to highlight aromatic species, whereas ammonia selectively ionizes compounds of high proton affinity, such as amines. The ionization of pollutants yields a mixture of pseudo-molecular ions which are subject to mass analysis by low resolution quadrupole mass filters.

The TAGA 3000, being a single quadrupole instrument, yields APCI mass spectra, which ultimately must be interpreted by an experienced TAGA scientist. The resultant pollutant identifications may be tentative, the degree to which depends upon the pollutant, the inherent selectivity of the ionization technique, and sample matrix. The difficulties of contaminant identification are greatly reduced by the superior analytical capabilities of the TAGA 6000.

The TAGA 6000, an APCI/MS/MS system, can rapidly speciate and quantify VOCs on site. The basic operating principle of the TAGA 6000 is sequential mass spectrometry: ions separated by the first quadrupole are fragmented with argon gas in a second quadrupole (RF only), and the fragment ions are analyzed by the third quadrupole. The collisionally activated decomposition (CAD) fragment ion spectra is compared to standard CAD library spectra. Thus the tandem mass spectrometer provides a much greater degree of specificity than the single MS system of the TAGA 3000.

The standard APCI source is particularly sensitive to polar compounds. Compounds previously measured by MAMU 3 include amines, amides, alcohols, sulfides, mercaptans, aldehydes, ketones, phenols, chlorophenols, acids and aromatic hydrocarbons. The real-time limits of detection for the TAGA 3000 range from 0.1 to 10  $\mu\text{g}/\text{m}^3$ , depending on the type of chemicals and the complexity of the sample matrix.

Both the TAGA units are equipped with a ten metre, telescopic tower and meteorological instrumentation to measure local wind speed, wind direction and ambient temperature. All meteorological data are stored by the on-board computer simultaneously with the

collection of air quality data. The meteorological data are updated every 30 seconds, allowing the operator to assess the data on site and apply it to the survey strategy.

The MAMU 3 vehicle is also a GMC Transmode. Instrumentation and other equipment in MAMU 3 are powered by two six-kilowatt generators with electronic frequency controllers. An Orion bus was selected as the host vehicle for the TAGA 6000. All the power requirements of the MAMU 4 is supplied by a 17.5 kilowatt generator. For a sketch of the floor plan see Figure 1b.

#### Survey Strategy

Over the past ten years, more than 120 air monitoring surveys have been conducted by the Monitoring Instrumentation and Development Unit of the Air Resources Branch. During this period, a systematic approach to air monitoring has evolved based on the unique strengths (and limitations) of the MAMUs and the accumulated experience of the MAMU staff.

When planning and executing a survey strategy the following are considered:

- survey objectives
- type and description of environmental problem
- source inventory and production schedules
- monitoring capabilities and resources
- climatology
- local topography and accessibility
- real-time measurements of target compounds
- other neighbouring sources

Basically, the survey strategy is to acquire and analyze representative air samples downwind of the suspected source. To isolate the source, upwind samples are also collected. On occasion, concurrent upwind and downwind air sampling by MAMUs 1 and 2 is performed to key in on a particular source in a heavily industrialized area. Further delineation of the source is possible by correlating meteorological data with the ambient air quality data. A main advantage of using the MAMUs for pollution surveys is their ability to produce monitoring results in the field. The survey scientists can assess the monitoring strategy on site, and if necessary, alter it to achieve the required survey objectives. The duration of an air monitoring survey will depend on the nature of the environmental problem, the survey objectives, and the frequency occurrence of the preferred wind conditions. On average, the total survey period is about two weeks with a typical working day being 12 hours.

#### Field Applications

The analytical capabilities of the four MAMUs together provide

for the detection of a broad range of organic and inorganic pollutants. Practically every chemical class can be monitored with these sophisticated units (see Table 2). Their versatility allows for their application to an assortment of environmental concerns.

Air studies are initiated by the Ministry's six Regional Offices that request assistance in monitoring. The MAMUs have undertaken many monitoring tasks including regulatory monitoring, emergency response to chemical spills, assessing general air quality, identifying specific pollution sources, checking the effectiveness of industrial abatement measures, and odour source characterization.

These units have been used to investigate the emissions from a variety of industrial sources, for example, kraft mills, smelters, oil refineries, landfill sites, incinerators, steel mills, tar plants, generating stations, auto plants, and many types of chemical plants. MAMU 3 has responded to several environmental emergencies, such as the train derailments in Mississauga and Medonte, and most recently, the PCB warehouse fire in St. Basile Le Grand, Quebec.

Cited below are examples of some recent field studies which showcase the analytical capabilities of the MAMUs and the Ministry's on-site approach to the analysis of airborne contaminants.

#### EXAMPLE 1: Common Pollutants - MAMU 1

During one of the first air quality surveys undertaken by MAMU 1 (1978 Nanticoke), the on-site aspect of mobile monitoring was exemplified. At a downwind distance of 16 kilometres, fumigation of the Nanticoke generating station plume was monitored and the classical  $\text{NO}_x/\text{O}_3$  sink-source relationship of this  $\text{SO}_2$  plume was clearly revealed. Outside the fumigation area the ambient levels of  $\text{SO}_2$  and  $\text{NO}_x$  were below the Ministry Standards; ozone concentrations were above the Standard. As the plume passed overhead, the  $\text{O}_3$  concentration decreased from 0.12 ppm to 0.07 ppm, while there was a marked increase in  $\text{NO}_x$  (0.02 ppm to 0.10 ppm) and  $\text{SO}_2$  (0.05 ppm to 0.25 ppm). Today these pollutants are still used to track plumes to their point of impingement. This classical example of common pollutants behaviour is shown in Figure 4.

#### EXAMPLE 2: VOCs - MAMU 2

With the inclusion of a gas chromatograph (GC) system, the monitoring capabilities of MAMUs 1 and 2 were increased to include 133 volatile organic compounds (VOCs). Subsequently, the emissions could be chemically characterized, allowing source fingerprinting. For example, in 1987 MAMUs 1 and 2 conducted an extensive air quality survey in a highly industrialized area of Southern Ontario.

There was particular interest in three industries: a tar plant, a steel mill, and a foundry. The total VOCs averaged approximately 800  $\mu\text{g}/\text{m}^3$ , 600  $\mu\text{g}/\text{m}^3$ , and 250  $\mu\text{g}/\text{m}^3$  respectively. In comparison, the VOCs totalled 180  $\mu\text{g}/\text{m}^3$  in the nearby downtown area. The contribution of individual VOCs reveals significant differences in contaminant patterns for the various sources (see Figure 5). For instance, the highest levels of benzene were observed downwind of the tar plant, whereas the foundry was a major contributor of xylenes. Naphthalene was primarily detected in ambient air samples collected in the vicinity of the tar plant. Thus detailed knowledge of several VOCs can serve to fingerprint sources in a high density industrial area.

#### Example 3: VOCs - MAMU 3

This example demonstrates the importance of recording the meteorological data during the acquisition of contaminant levels. Figure 6 shows the real-time response to dimethyl sulfide (DMS) which was monitored downwind of a pulp and paper mill. A revealing feature in this Figure is that the instantaneous levels of DMS surged between the 6 and 10 minute mark while the wind speed and direction remained relatively constant. Apparently this episode of DMS was due to the purging of the digesters at the mill. The short-term level approached 120 ppb, roughly ten times the time-weighted-average, certainly high enough to cause an obnoxious odour in the immediate vicinity. Note that conventional trapping methods would not have been able to fully characterize this phenomenon for they do not reveal temporal distributions.

#### Example 4: VOCs - MAMU 3 and MAMU 4

During the spring of 1983, the mobile TAGA 3000 conducted an air monitoring study in response to odour complaints in the vicinity of a rubber chemicals plant. Aniline and benzothiazole were identified from the mass fingerprints. A mobile survey was undertaken where these compounds were measured while the TAGA criss-crossed the streets immediately downwind of the plant. The real-time response to these contaminants is shown in Figure 7. From these data it is apparent that both aniline and benzothiazole originate from the same source, in fact, they were tracked to the same building as clearly indicated by the aniline isopleth map. This data also shows the plume concentrations as a function of distance, or the dispersion characteristics which may be helpful for planning the location of stationary VOC monitoring equipment.

In August 1988, the mobile TAGA 6000 (MAMU 4) returned to this area to test the identification capabilities of MS/MS. The CAD spectra for masses 136 and 94 (see Figure 8) were searched against the library of standard spectra. The two contaminants, aniline and benzothiazole, were the same two identified downwind of this source five years previously using the TAGA 3000.



Once the compounds have been identified it is possible to ascertain the levels of specific contaminants by recording the real-time response to two or more parent/daughter ion pairs. Figure 9 shows the data recorded for ambient levels of aniline using the parent/daughter ion pairs of 94/77 and 94/51. Note the excellent agreement in the concentration profiles.

#### Laboratory Support

##### Evolution of GC Technology for VOC Analysis

Between 1979 and 1981, the Air Resources Branch was involved in developing a program to collect, detect and determine polychlorinated biphenyls (PCBs) in ambient air. Samples collected on florasil cartridges were analyzed on a GC with a packed glass column preceded by a rigorous solvent extraction and clean-up procedure. The glass column was 3.6 m X 2 mm ID X 6 mm OD containing 1% Derosil 400 on Anakrom A 90/100 mesh. An EC detector was used for its selective sensitivity towards halogenated compounds.

Although retention times were stable and peak areas were relatively constant, the columns exhibited a highly variable baseline, particularly at higher temperatures. More importantly, the resolution provided by packed columns was inadequate. This was proven when several samples were rerun on capillary GC columns, and large peaks were resolved into several multiple peaks. It was determined that packed columns significantly overestimated the levels of PCBs in ambient air. The new fused silica capillary columns developed by Hewlett-Packard were selected due to their advantages over both packed and glass capillary columns. These advantages include flexibility, inertness, thermal stability, high efficiency and inherent straightness. In the first quarter of 1980 analyses were performed using 0.2 mm ID 25 m column coated with SP2100 on an HP 5840 GC with an ECD detector. Although greatly improved, the co-elution of impurities with the PCB isomers still existed, due to the complexity of the sample matrix.

The next stage in the development involved converting the system to a dual capillary column analyzer. A sample was split and passed through two columns differing in polarity. Co-elution of peaks that occurred on one column were, in many instances, resolved on the other, thus improving the quantitation of PCB isomers by an order of magnitude over single capillary analysis. Two sets of columns were used: SP2100-/Carbowax 20M, and OV-1-/SE54. The initial combination was eventually discarded due to its inadequate temperature limit of 220°C. The columns, a combination of OV-1-/SE-54, were prototypes from Hewlett-Packard with a temperature limit of 350°C. Further improvements in column stability have been brought about through the development of

cross-linking techniques.

The dual column techniques were accelerated using a new and advanced GC: HP 5880A equipped with dual EC detectors. The computer's additional memory afforded more accurate quantitation programmes, based on Kovat's theory of retention indices, in place of the less reproducible retention times.

Measurement of VOCs in a mobile laboratory situation began after the completion of the PCBs work in 1980. Injecting a large gas volume quantitatively into a gas chromatograph has always presented problems, particularly when using capillary columns. In order to prevent a loss of column efficiency, the sample must be introduced to the column as an infinitely narrow band. To achieve this, a pre-focusing step is required to increase the concentration of trace components and reduce sample volume.

Sample concentration was achieved by using an adsorbent cartridge. Two basic extraction techniques, solvent and thermal desorption, were available. Direct thermal desorption of the adsorbent cartridge was selected because of its inherent advantages over solvent desorption: speed (no sample preparation); the entire sample is analyzed; there are no solvent peak interferences; contamination introduced during sample clean-up is eliminated; it can be easily automated for repetitive sampling; and its simplicity of operation is conducive to field work.

The next step involved introducing the sample to the GC column in a narrow band. With the introduction of capillary columns, the direct desorption of a relatively bulky adsorbent onto the column was not feasible. Desorption gas flows of 5 - 30 ml/min. for 15 minutes were required to completely remove the VOCs from the adsorbent. The gas flow to the capillary column, typically 0.5 - 2 ml/min., would require an extremely long time for complete desorption. A trapping interface was therefore required that allowed removal of analytes under high gas flow, held them in a narrow band and then transferred them to the capillary column under low (carrier) gas flow conditions.

The method selected was cryogenic focusing. The cartridge is desorbed with an inert gas (helium) at 10 - 30 ml/min. through a 0.04" ID nickel capillary, cooled with liquid nitrogen. The sample components are condensed in the small volume of the nickel loop, then heated ballistically to pass the sample onto the capillary column as quickly as possible. The GC column is cooled to -50 °C to maintain the sample in a narrow band. The system, now automated and operated routinely in MAMUs 1 and 2 and the laboratory, can also handle cartridges collected remotely.

Presently, the system contains a water dryer (Napion, perma-pure), a system based on permeation distillation to remove water from the sample before it enters the nickel capillary.



Unfortunately this system also removes oxygenated and other polar compounds from the sample stream. Therefore, the classes of compounds currently being quantified are restricted to the aliphatic, aromatic, and chlorinated hydrocarbons.

An example of a chromatograph obtained with the present GC system is shown in Figure 10. The analysis of an air sample taken downwind of a tar plant in 1985 indicates the presence of several VOCs with the major components being aromatic hydrocarbons. At the time of this particular survey, naphthalene was not in the retention index library and consequently the large peak at 20.30 minutes was initially unidentified. Since this peak accounted for 22 per cent of the total area, identification of this unknown was imperative. Cartridge samples collected at this site with a portable sampler were later analyzed using a Hewlett-Packard Mass Selective Detector (MSD). The best match chosen by the library searching algorithm was naphthalene. In later surveys of the same source naphthalene levels were quantified (see Figure 2).

#### Hyphenated Techniques

New hyphenated techniques are currently under development in the laboratory to improve upon the positive identification of volatile organic compounds. A system is now in place that includes three capillary columns, two connected to flame ionization detectors and the third to a mass selective detector (see Figure 2). Mass spectral data are often used to help positively identify sample components. Other hyphenated techniques in the development stage are dual oven (GC/GC) gas chromatography and GC/FTIR. The latter will be used as an identification tool in a similar manner to the mass selective detector.

#### Multidimensional Gas Chromatography

Techniques using multidimensional gas chromatography are being developed to improve the resolution of compounds in a complex mixture which is typical of airborne contaminants. Even though recent improvements in column technology have produced capillary columns which approach the theoretical limits of efficiency, a single column is usually not able to resolve all the compounds in an airborne sample. Consequently, the use of two different columns connected in parallel or in series, known as multidimensional gas chromatography, is being applied to address this problem. The series approach is being studied, whereby the first column is used for the initial separation and a selected portion of the elutant is transferred, by flow switching, to a second column of different polarity for enhanced separation.

This work is being performed on a Siemens Sichromat 2 gas chromatograph which has two independently controlled ovens, one

for each column, allowing the separate temperature programming of the two columns. Presently a microwave desorber unit is being adapted to the Sichromat for the purposes of rapidly vaporizing of organic compounds into the gas chromatograph. A further enhancement of this system will be the addition of a mass selective detector to improve identification of unknown contaminants.

#### GC/MI/FTIR

The recent marriage of Fourier Transform Infrared (FTIR) spectroscopy and low temperature matrix isolation (MI) is proving to be an exceptional technology to reliably identify environmental contaminants emerging from a gas chromatograph. The Air Resources Branch laboratory has recently procured a Cryolect 4800 or GC/MI/FTIR. This instrument will significantly improve the capabilities of identifying trace VOCs. At present, the Cryolect system is being evaluated using the 133 compounds targeted by the GC systems of MAMUs 1 and 2.

The enhanced sensitivity and specificity of the Cryolect 4800 is due to the isolation of the GC elutants in an argon matrix held at a nominal temperature of 12 K. The gas chromatograph fractions are mixed with argon and rapidly frozen onto a rotating disk. Then the frozen fractions are rotated into the optical path of the FTIR spectrometer where the IR spectra are generated. The fact that each sample molecule is trapped in a solid argon cage leads to very narrow, intense adsorption bands.

Trapping the sample on the cold disk allows for repetitive scanning up to 5000 times, subsequently increasing the signal-to-noise ratio and improving the sensitivity. Most infrared absorbers of medium strength are detectable at the sub nanogram levels.

With the high resolution provided by the MI/FTIR system it is possible to distinguish between compound isomers. Figure 11 shows the infrared spectra of the three isomers of dimethylxylene: ortho-, meta- and para-xylenes. The spectral peculiarities are obvious and are particularly valuable for distinguishing between meta- and para-xylenes, which usually co-elute on high resolution GC systems.

Another positive feature of the GC/MI/FTIR is the spectral deconvolution of partially merged compounds. Known library spectrum of one of the suspected compounds is subtracted from the sample spectrum and the resultant spectra is subjected to library search techniques, leading to the identification of the unknowns. An example of the spectral deconvolution technique is shown in Figure 12. The two co-eluting compounds were hexane and trichloroethene. Hexane started to elute first and an infrared spectrum was taken at 16.74 minutes (see Figure 12ii). At 17.19 minutes a trichloroethene peak co-eluted with hexane yielding a mixture. As clearly seen in Figure 12iii, the infrared spectrum

displays features of both hexane and trichloroethene. However, when the hexane spectrum was subtracted from the mixture spectrum, the signature of trichloroethene is clearly evident (see Figure 12i).

#### Future

The identification, detection and quantitation of trace organic compounds in air is a complicated task, just in the infancy stages of development. An estimated 40,000 chemicals are manufactured worldwide on an industrial scale. Furthermore the number of chemicals produced as byproducts is an unknown factor. It is estimated that the number of compounds present in a sample of clean air in concentrations of low  $\mu\text{g}/\text{m}^3$  or less total some  $10^4$  to  $10^6$  organic compounds.

The complex chromatogram of Figure 13 is indicative of an air sample containing a high number of volatile organics. Although the total organic loading was approximately  $400 \mu\text{g}/\text{m}^3$ , the large number of unresolved peaks limits the effectiveness of the dual column GC technique. This particular chromatogram represents a 30 litre sample recently collected with a three stage cartridge downwind of a waste oil refinery. Of the 178 peaks detected, only 84 were identified. Moreover, the identification of these compounds is tentative because of the lack of baseline resolution and the obvious co-elution of several compounds. A possible solution to this unfortunate phenomenon is to heart cut a portion of the sample with a second column, identify peaks and subject the elutants to more sophisticated techniques such as MS/MS or FTIR.

In addition to the current work, the Air Resources Branch laboratory is studying advanced techniques of sample concentration, separation and detection; namely, the application of GC/GC, GC/MI/FTIR and MS/MS. Eventually, the FTIR will be integrated with a multidimensional gas chromatograph and a MSD producing the optimal analytical system. Simultaneous output from the detectors will be computer correlated to give unequivocal identification of trace VOCs.

Another program in the early stages of development is diffusion sampling. Semipermeable silicone membranes will be used to test their efficacy in separating both polar and nonpolar compounds from water. Eventually this research may lead to a solution to the inherent water problems associated with cryogenic concentration techniques of the current GC system.

Future plans for MAMUS 1 and 2 include the possible installation of a MSD to improve compound identification. There are also plans to integrate a GC with the TAGA 6000 to permit the analysis of adsorbent cartridges. This may enhance the capabilities for rapid analysis of soils and water samples for toxic contaminants. In addition, a program will be undertaken to

expand the scope of compounds detectable by the TAGA 6000 by replacing the APCI source with the low-pressure CI. Preliminary studies indicate the low-pressure CI source is more sensitive toward chlorinated and aromatic hydrocarbons.

#### ACKNOWLEDGEMENTS

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CHEMICAL COMPOUND LIST FOR MOBILE AIR MONITORING UNITS #1 AND #2

ARB Mobile Air Monitoring Unit (MAMU-1)

Table 2:

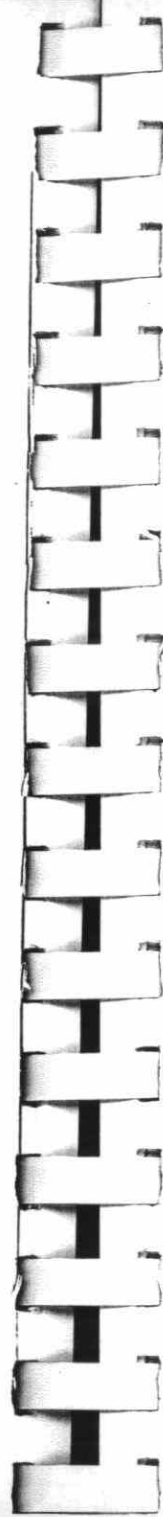
# SUMMARY OF THE MAMU'S ANALYTICAL CAPABILITIES TYPE OF COMPOUNDS DETECTED AT TRACE LEVELS

## MAMUs 1 and 2

- classical pollutants  
(e.g. NOx, CO, SO2, TRS,  
O3, THC, etc.)
- C3 to C12 non-polar hydro-  
carbons including alkanes,  
alkenes, alkynes, aromatic,  
and chlorinated hydrocar-  
bons.

## MAMUs 3 and 4 (TAGA)

- polar compounds including  
amines, amides, acids, al-  
dehydes, alcohols, ketones,  
esters, phenols, sulfides,  
mercaptans, chlorinated  
aromatics, etc.
- inorganic acids, halides



## ARB VOC ANALYSIS SYSTEM

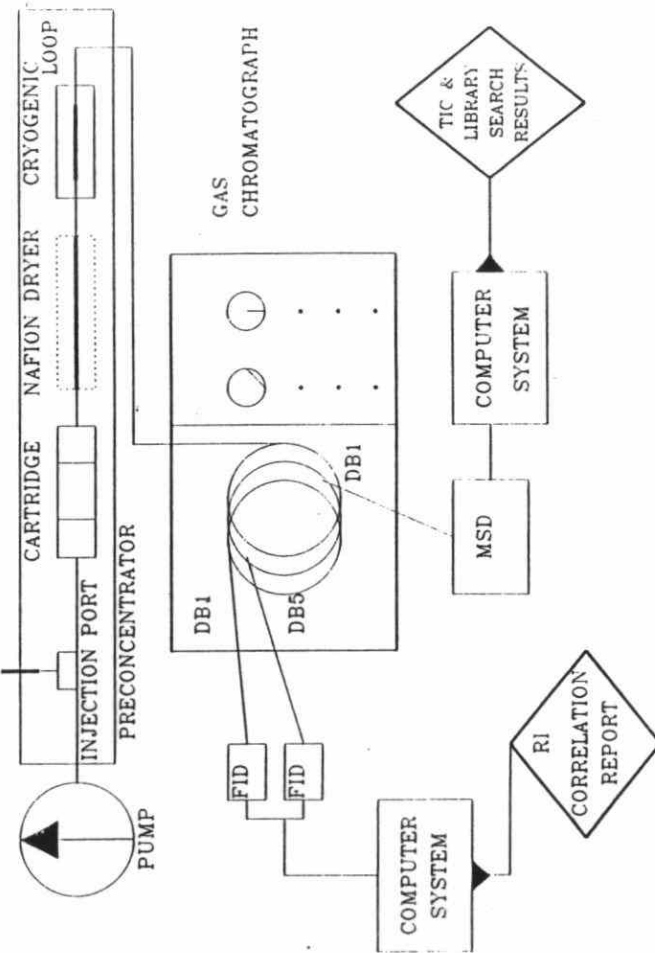


Figure 2:

## MOE TAGA 6000E FRONT END AND VACUUM CHAMBER

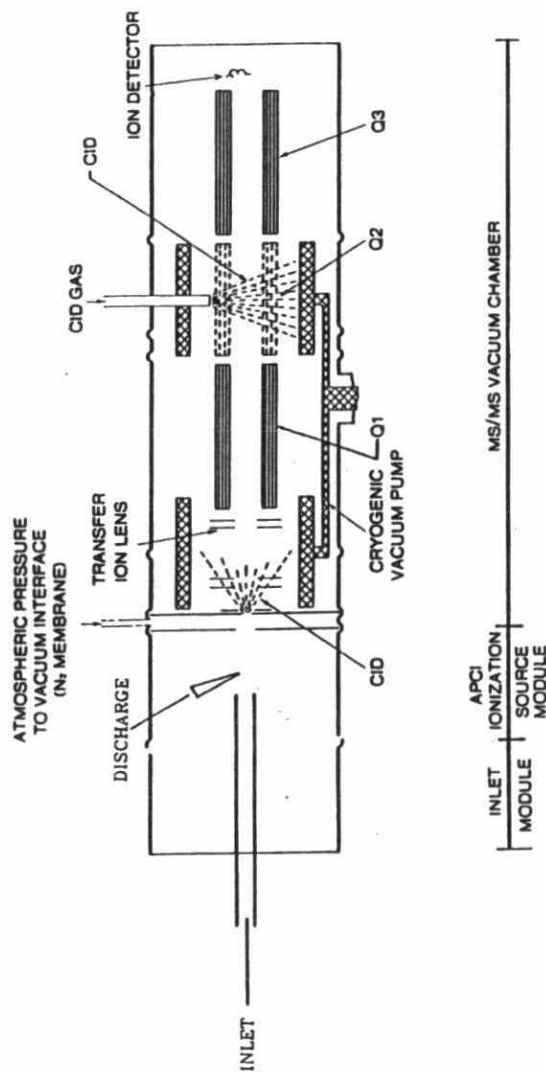
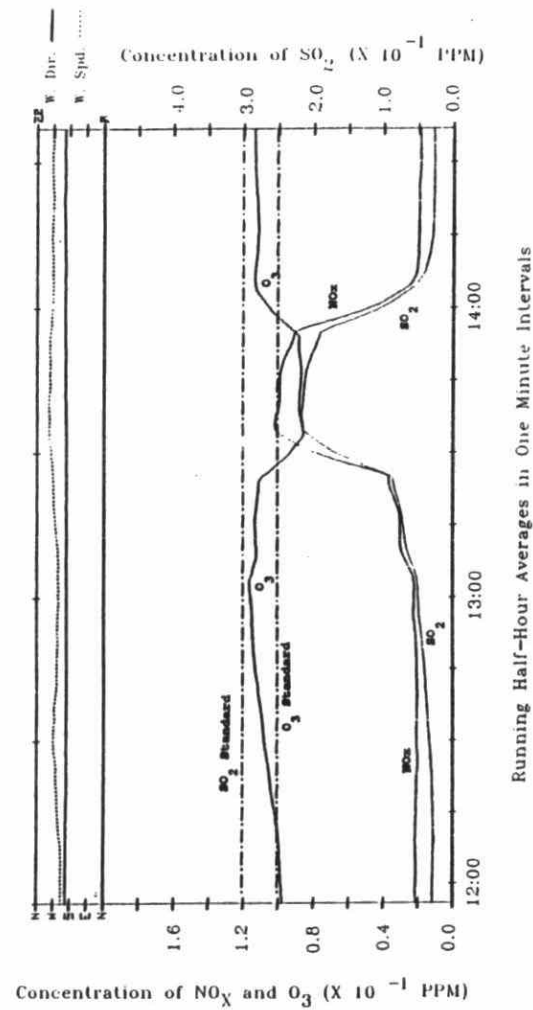


Figure 3:

# AIR RESOURCES BRANCH MAMU 1 NANTICOKE (1978) COMMON POLLUTANTS

Figure 4: Ambient levels of  $\text{SO}_2$ ,  $\text{O}_3$ , and  $\text{NO}_x$  recorded by MAMU 1 in Nanticoke, 1978.

# Mobile Air Monitoring Unit #1 Source Partitioning

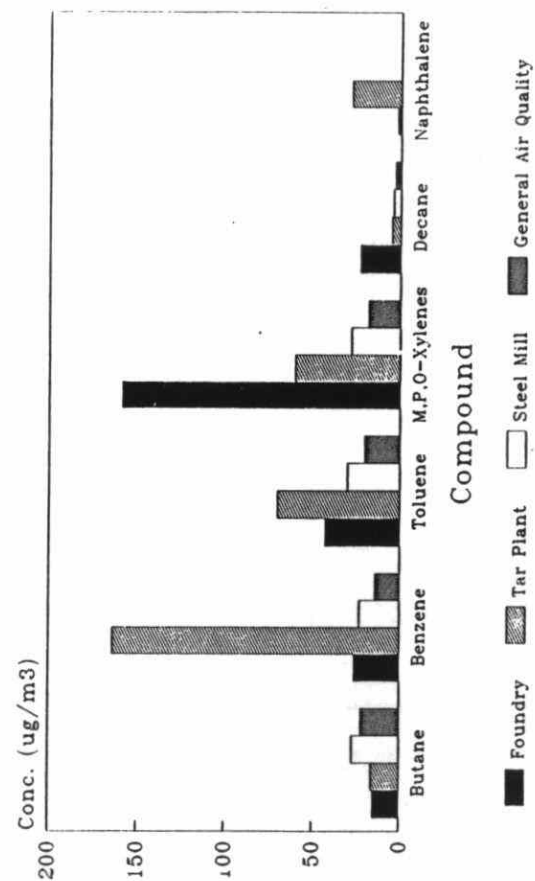


Figure 5: Source partitioning of selected VOCs  
MAMUs 1 (and 2) Industrial Complex 1987.

## Dimethylsulfide vs. Meteorological Data

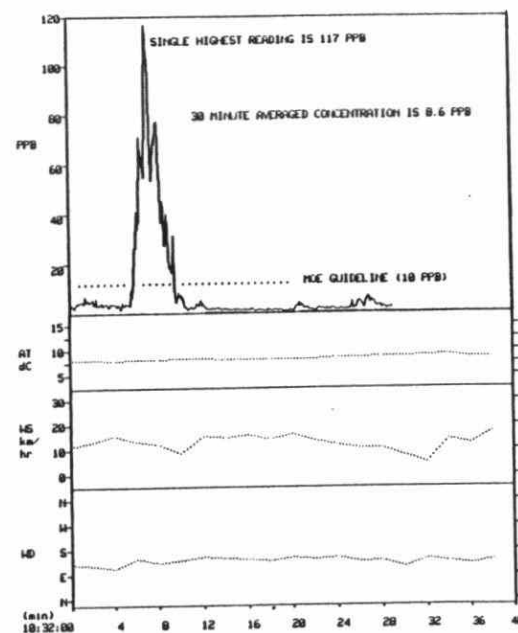
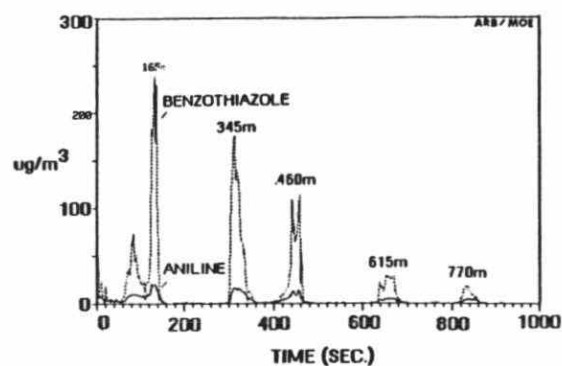
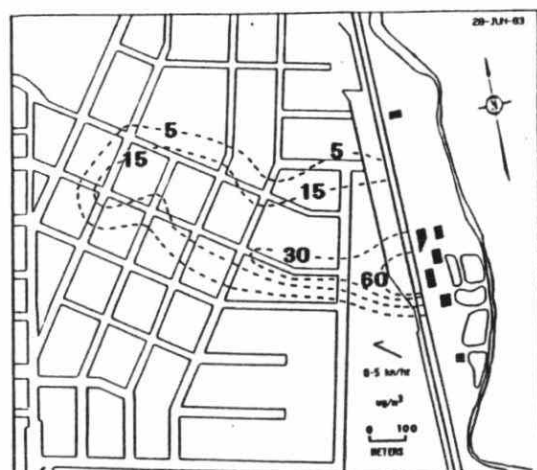


Figure 6: Real-time monitoring of dimethyl sulfide downwind of a paper mill while simultaneously monitoring meteorological data.



Figure 7  
ANILINE ISOPLETHS (CHEMICAL PLANT)



MOE TAGA 6000 Field Test 1, August 1988

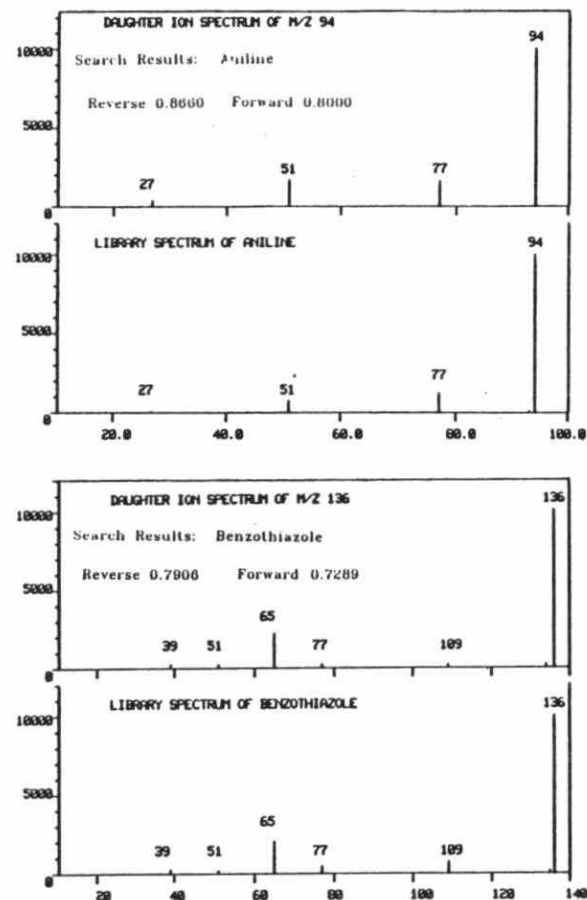


Figure 8: MOE TAGA 6000 search results for CAD spectra parent ions 94 (top) and 136 (bottom). Chemical rubber plant (August 1988).

MOE TAGA 6000 Field Test 1, August 1988

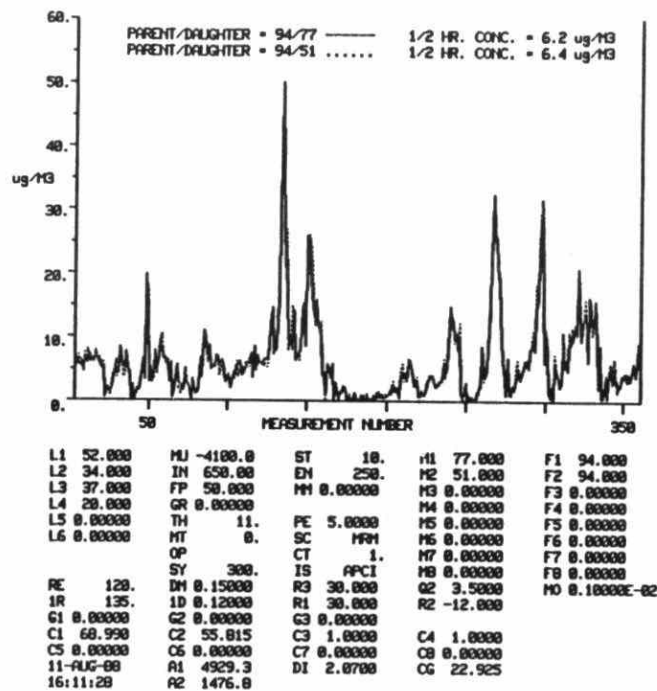


Figure 9: MOE TAGA 6000 instantaneous measurements of aniline using two daughter ion pairs (94/77 and 94/51).  
Note: the excellent agreement in the calculated 1/2-hour averages for the two parent daughter ion pairs.

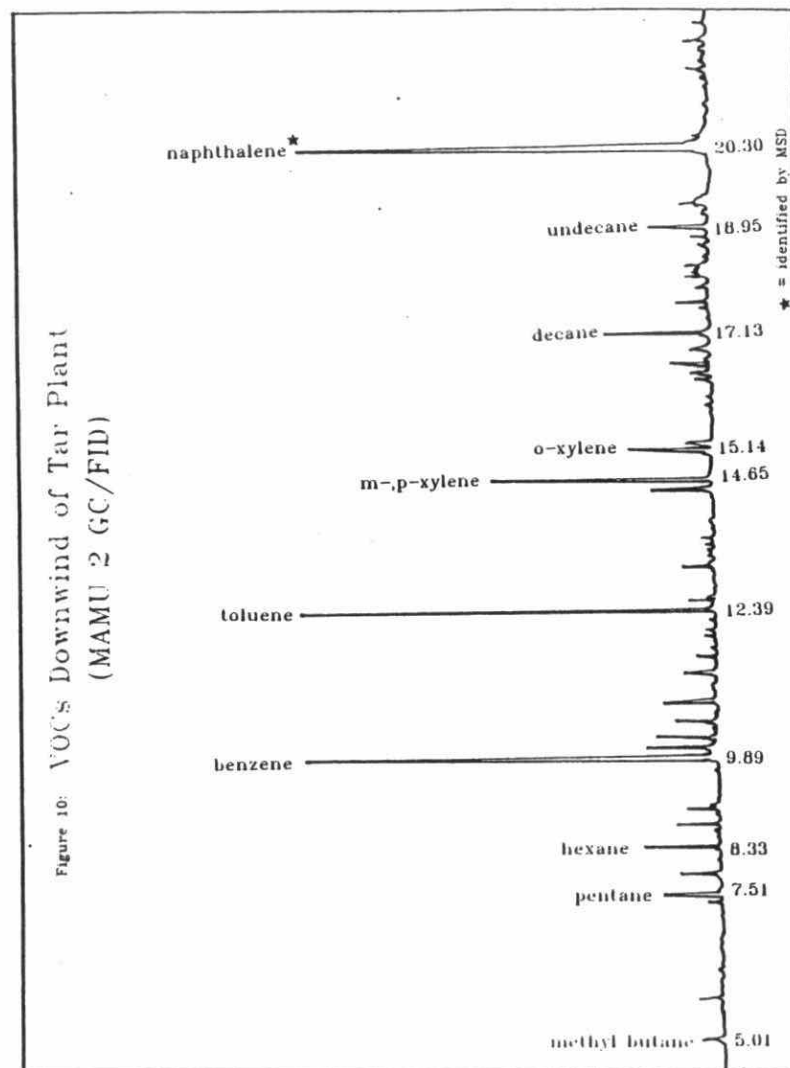


Figure 10: VOCs Downwind of Tar Plant (MAMU 2 GC/FID)

Figure 11: SPECIATION OF DIMETHYL BENZENE ISOMERS

BY GC/MI/FTIR

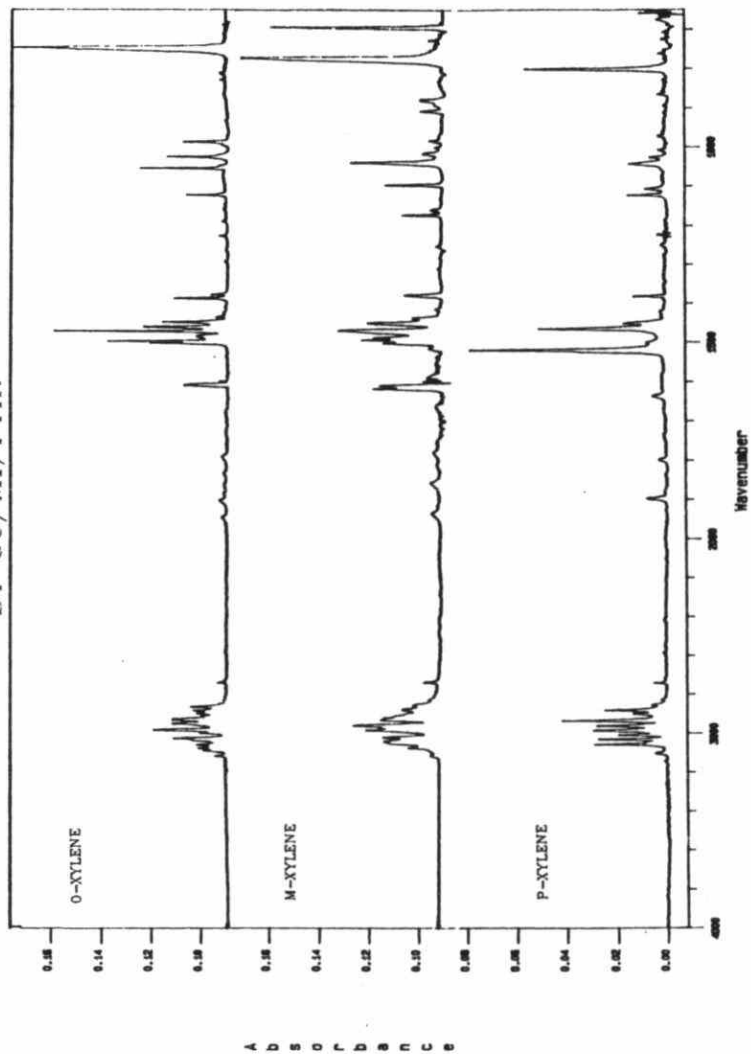
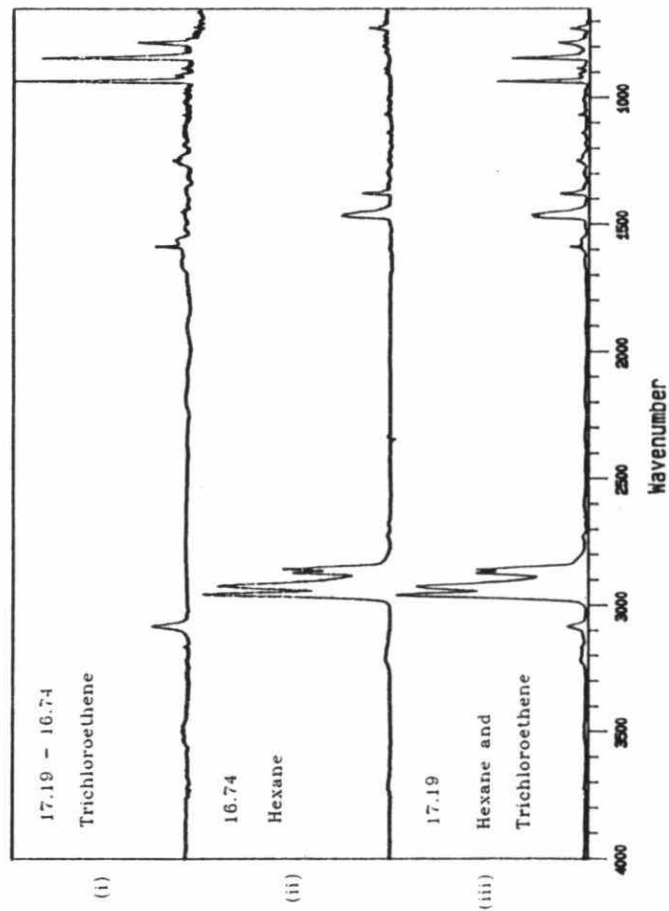


Figure 12: SPECTRAL DECONVOLUTION OF MERGING COMPOUNDS  
BY GC/MI/FTIR



**Figure 13:**

